Supplementary Information for

Position-specific and Clumped Stable Isotope Studies: Comparison of the Urey and Path-Integral Approaches for Carbon Dioxide, Nitrous Oxide, Methane, and Propane

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Table S - 1: Partition function ratios and equilibrium constants calculated using PIMC. Statistical errors are in parentheses and apply to the last digit.

T (K)	$\Delta_{^{16}O^{13}C^{18}O}$-HB			$\Delta_{^{16}O^{13}C^{18}O}$-LB		
	$R_{^{16}O^{12}\rightarrow^{13}C^{16}O}$	$R_{^{16}O^{12}\rightarrow^{13}C^{18}O}$	K	$R_{^{16}O^{12}\rightarrow^{13}C^{16}O}$	$R_{^{16}O^{12}\rightarrow^{13}C^{18}O}$	K
300	1.34246(8)	1.34374(7)	0.99904(8)	1.340520(9)	1.341808(9)	0.999040(9)
400	1.26788(3)	1.26861(5)	0.99942(5)	1.26634(1)	1.267067(9)	0.99943(1)
500	1.22730(2)	1.22774(5)	0.99964(4)	1.225898(6)	1.226335(6)	0.999643(7)
600	1.20224(6)	1.20254(3)	0.99975(6)	1.201292(4)	1.201571(3)	0.999768(5)
T (K)	$\Delta_{^{14}N^{15}N^{16}O}$			$\Delta_{^{13}CH_3D}$		
	$R_{^{14}\rightarrow^{15}N^{14}N^{16}O}$	$R_{^{14}N^{14}\rightarrow^{15}N^{16}O}$	K	$R_{^{12}\rightarrow^{13}CH_4}$	$R_{^{12}\rightarrow^{13}CH_3D}$	K
300	1.25485(7)	1.19879(8)	0.95533(8)	1.25495(4)	1.26215(5)	0.99429(5)
400	1.20456(5)	1.16818(8)	0.96980(8)	1.21374(4)	1.21799(3)	0.99651(4)
500	1.17666(6)	1.15091(7)	0.97812(7)	1.19024(1)	1.19297(4)	0.99771(3)
600	1.15954(7)	1.14014(7)	0.98327(7)	1.17547(4)	1.17725(3)	0.99849(4)
T (K)	$\Delta_{^{12}CH_3{}^{12}CHD{}^{12}CH_3}$			$\Delta_{^{12}CH_3{}^{13}CH_2{}^{12}CH_3}$		
	$R_{1\rightarrow^2H_t}$	$R_{1\rightarrow^2H_c}$	K	$R_{1\rightarrow^2C_t}$	$R_{1\rightarrow^2C_c}$	K
300	32.412(8)	29.505(9)	0.9103(4)	1.29398(3)	1.27525(5)	0.98553(4)
400	14.647(3)	13.887(4)	0.9481(3)	1.23400(3)	1.22403(2)	0.99192(3)
500	9.282(2)	8.975(2)	0.9669(2)	1.20158(3)	1.19602(3)	0.99538(3)
600	6.946(1)	6.794(1)	0.9781(2)	1.18212(1)	1.17877(2)	0.99716(2)

Table S - 2: Calculated normal mode wave numbers for CO_2 isotopologues

$\bar{\omega}$ (cm^{-1})	$^{16}O^{12}C^{16}O$	$^{16}O^{13}C^{16}O$	$^{16}O^{12}C^{18}O$	$^{16}O^{13}C^{18}O$
$\bar{\omega}_1$	672.8652	653.7147	667.7360	648.4339
$\bar{\omega}_2$	672.8652	653.7147	667.7360	648.4339
$\bar{\omega}_3$	1353.6090	1353.6090	1314.5261	1314.4491
$\bar{\omega}_4$	2396.2675	2328.0668	2378.4771	2309.7949

Calculated from potential energy surface given by Zúñiga et al., *J. Mol. Spectrosc.* **1999**, *195*, 137–146

Table S - 3: Calculated normal mode wave numbers for N_2O isotopologues.

$\bar{\omega}$ (cm^{-1})	$^{14}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{15}N^{14}N^{16}O$
$\bar{\omega}_1$	596.3070	582.6763	592.7572
$\bar{\omega}_2$	596.3070	582.6763	592.7572
$\bar{\omega}_3$	1298.2802	1296.4726	1281.2784
$\bar{\omega}_4$	2282.1801	2232.9808	2259.4610

Calculated from potential energy surface given by Zúñiga et al., *J. Chem. Phys.* **1999**, *110*, 6339–6352

Table S - 4: Calculated normal mode wave numbers for methane isotopologues.

$\bar{\omega}$ (cm^{-1})	$^{12}CH_4$	$^{13}CH_4$	$^{12}CH_3D$	$^{13}CH_3D$
$\bar{\omega}_1$	1345.3267	1336.9620	1188.0862	1179.9753
$\bar{\omega}_2$	1345.3267	1336.9620	1188.0862	1179.9753
$\bar{\omega}_3$	1345.3267	1336.9620	1339.8201	1332.5799
$\bar{\omega}_4$	1570.3634	1570.3634	1508.0909	1507.0911
$\bar{\omega}_5$	1570.3634	1570.3634	1508.0909	1507.0911
$\bar{\omega}_6$	3036.1496	3036.1496	2285.1892	2273.9839
$\bar{\omega}_7$	3157.0668	3145.8475	3071.4074	3067.7074
$\bar{\omega}_8$	3157.0668	3145.8475	3156.7900	3145.5356
$\bar{\omega}_9$	3157.0668	3145.8475	3156.7900	3145.5356

Calculated from potential energy surface given by Lee et al., *J. Chem. Phys.* **1995**, *102*, 254–261

Table S - 5: Zero-point energies (cm^{-1}) for Urey-AHO calculations.

$\Delta_{^{16}O^{13}C^{18}O}$		$\Delta_{^{14}N^{15}N^{16}O}$		$\Delta_{^{13}CH_3D}$	
Isotopologue	E_0	Isotopologue	E_0	Isotopologue	E_0
$^{16}O^{12}C^{16}O$	2525.394	$^{14}N^{14}N^{16}O$	2370.470	$^{12}CH_4$	9638.564
$^{16}O^{13}C^{16}O$	2472.905	$^{14}N^{15}N^{16}O$	2331.890	$^{13}CH_4$	9610.417
$^{16}O^{12}C^{18}O$	2492.277	$^{15}N^{14}N^{16}O$	2347.310	$^{12}CH_3D$	9032.497
$^{16}O^{13}C^{18}O$	2439.355	—	—	$^{13}CH_3D$	9002.365